Real time GISAXS study of micelle hydration in CTAB templated silica thin films

S. Dourdain[a], A. Rezaire[a], A. Mehdi[b], B.M. Ocko[c], A. Gibaud[a,c],*

[a]*Université du Maine, Faculté des Sciences, UMR 6087 CNRS, 72085 Le Mans France*
[b]*Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637 CNRS, Université de Montpellier II, Place E. Bataillon, F-34095 Montpellier Cedex 5, France*
[c]*Department of Physics, Brookhaven National Laboratory, L.I. New-York 11973, USA*

Abstract

We have used grazing incidence small angle X-ray scattering (GISAXS) experiments to probe the mesoscopic organization of cetyltrimethyl ammonium bromide (CTAB) templated silica thin films combined to optical interferometry to monitor the macroscopic evolution of these films as a function of relative humidity (RH). The combination of these two experiments permits to address how water can penetrate or quit the silica network during cycling the RH. We report both the fast and the long time responses of these hybrid materials upon cycling the RH. We show that at high RH a hydration layer of one water molecule covers the micelles. Long time response evidences that the silica network remains flexible along the normal to the films for several hours.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Due to their wide use in catalysis, separation and sensors, new strategies and techniques are constantly developed to synthesize and to analyze the structure of mesoporous materials [1]. Surfac-

tant templated silica materials discovered by the researchers of the Mobil corporation are among the most studied examples of powdered mesoporous materials [2,3]. As shown by Brinker [4], the evaporation induced self-assembly (EISA) can be efficiently used to make these materials in thin films. The role of water in the fabrication of these films is of crucial importance because water is essential to ensure the hydrolysis of the silica precursor but also in promoting the micelle

*Corresponding author. Université du Maine, Faculté des Sciences, UMR 6087 CNRS, 72085 Le Mans France.

E-mail address: alain.gibaud@univ-lemans.fr (A. Gibaud).

formation. In addition water is inevitably present at the surface of self-organized assemblies and plays a critical role in the structure, stability and function of these systems. Computer simulation as well as ESR measurements carried out on micelles show that micelles are surrounded by a rather thin layer of water, typically 1–3 layers thick [5]. Thus, the study of the hydration layer turns out to be rather difficult. Particularly, water molecules can form a hydrogen bonded layer, called a hydration shell that surrounds hydrophilic substances. This shell adheres so powerfully that it is actually more energetically favorable for many polar substances to exist as individual molecules surrounded by hydration shells than to remain within a homogeneous solid material. In silica thin films templated by surfactant molecules, water can be found either in the silica network or at the surface of the micelles. Our aim was to study the influence of RH immediately after the formation of silica thin films templated by CTAB surfactant in order to address how water can penetrate or quit the silica network during cycling the RH. We report in the following how real-time GISAXS experiments combined to visible optical interferometry can provide useful information to understand the intrusion and extrusion of water in these materials.

2. Experimental

A sol containing surfactant, silica precursor, ethanol, water and hydrochloric acid (initial molar composition 1 TEOS:20 C_2H_5OH:5.4 H_2O:0.004 HCl:0.16 CTAB) was dispensed on to a Si(1 0 0) substrate. Only one drop (about 10 μl) of the initial sol was used so as to wet entirely the surface of the $2\,cm^2$ silicon wafer. After evaporation, the film was ~100 nm thick. The substrate was placed into the X-ray evaporation cell in which the humidity was controlled by flowing either dry or humid nitrogen. On the contrary to our previous measurements in which we did not measure precisely the RH, we have used in this study a humidity sensor (HC-610 from Ohmic) having a fast response allowing us to correlate the structural evolution to the RH. In particular, the RH was monitored in synchronization with the X-ray GISAXS data.

The GISAXS measurements were performed on the liquid spectrometer of the X22B beam line of the NSLS (National synchrotron Light Source, BNL, USA). The sample was kept horizontal during the course of the measurements and the incident beam was deflected by a Ge monochromator, so that it could impinge at a controlled incident angle on the surface of the liquid film slightly above the critical external angle of the silicon. The incident wavelength was fixed to 1.576 Å and the scattering was monitored with a MAR CCD 2D detector located 0.76 m away from the sample. Each frame was collected during a typical time of 20 s. Simultaneously the total thickness of the film was measured by optical interferometry with a multiple wavelength spectrometer (Filmetrics) working in normal incidence. The reflectance of the film could be measured in less than 1 s. The experiments were performed for more than 2 h. During this period of time, the RH was cycled sequentially. The response of the dry film during the cycling of RH was, thus, monitored over fast and very long periods.

3. Results and discussion

The effects of RH cycling are illustrated by the sequence of GISAXS patterns shown in Fig. 1. The first pattern taken after complete ethanol evaporation at $t = 500\,s$ and RH = 2.9% shows a 2D hexagonal phase of p6m symmetry (Fig. 1a, for more details about this phase see Refs. [6–9]). The RH was maintained for about 700 s to 2.9% so as to stabilize the 2D hexagonal phase. Indeed in the early stages of the film formation, raising the RH yields a phase transformation from the 2D hexagonal phase to the 3D Pm3n cubic phase [10]. This phase transformation is related to the high flexibility of the silica network and to the ability of water to intercalate between the head groups of the micelles. The period of time we have been waiting for, was in this case sufficient to avoid this transformation. Fig. 1b shows the GISAXS pattern at $t = 1000\,s$ for a RH of 84%. At this RH, it is clear that the 2D hexagonal lattice has undergone a very large swelling due to water intrusion. This is the signature that the silica
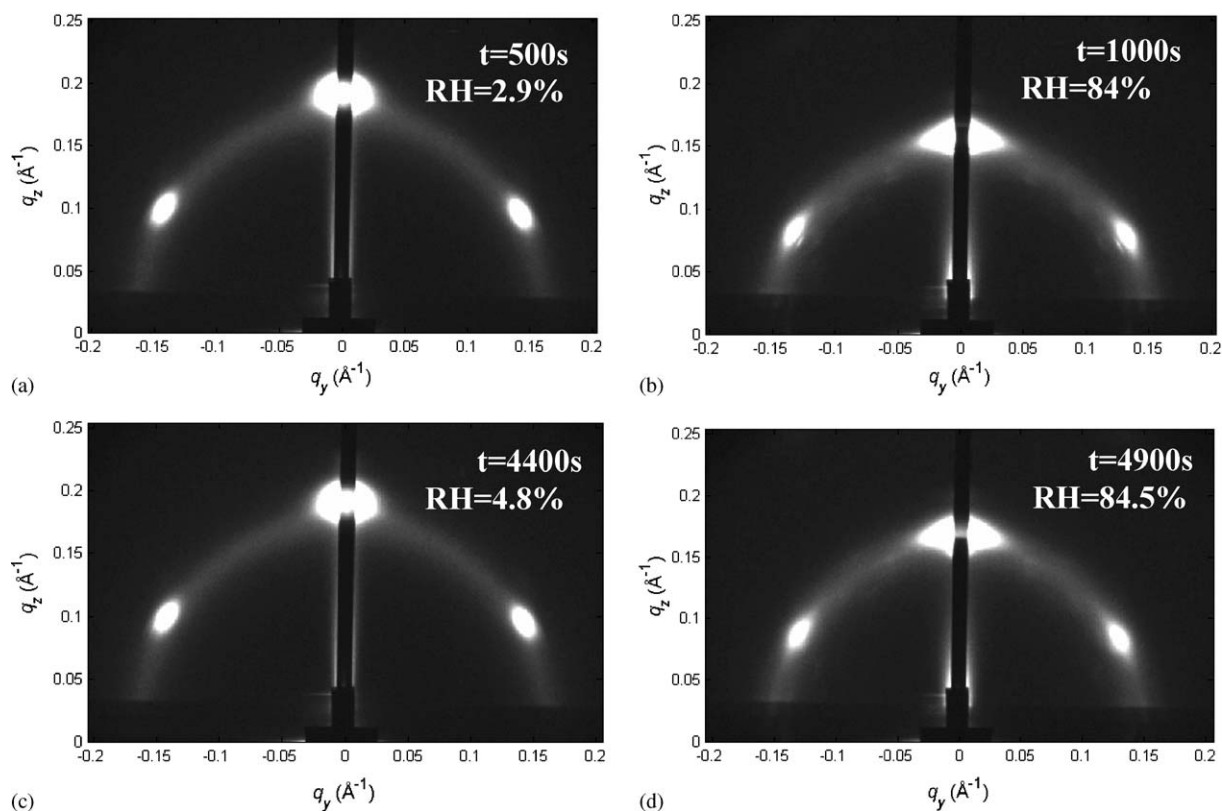
Fig. 1. GISAXS patterns showing the 2D hexagonal phase and its evolution during the humidity cycling: (a) 2D hexagonal phase at low humidity (RH = 2.9%, $t = 500$ s); (b) 2D hexagonal phase at high humidity (RH = 84%, $t = 1000$ s); (c) 2D hexagonal phase at low humidity (RH = 4.8%, $t = 4400$ s); and (d) 2D hexagonal phase at high humidity (RH = 84.5%, $t = 4900$ s). The 2D hex structure still expands or contracts with the humidity cycles 2 h after the complete evaporation of the solvent.

matrix is very flexible even after complete evaporation of the solvent. This is further evidenced in the two patterns taken at $t = 4400$ and 4900 s (Figs. 2c and d) in which one can see that the lattice still shrinks or swells when the RH is, respectively, low and high. However, after the first humidity cycle the 2D hexagonal lattice becomes distorted. After the first humidity cycle the 2D hexagonal lattice becomes distorted. Therefore instead of using the 2D hexagonal unit cell, we have been working in the framework of a rectangular face-centered unit cell described by the two lattice parameters b and c (for details see Refs. [6–9]). In the rectangular face-centered unit cell, the typical $(1\,0)_{Hex}$ and $(0\,1)_{Hex}$ 2D hexagonal Bragg reflections correspond to the $(1\,1)_{rec}$ and $(0\,2)_{rec}$ reflections, respectively.

The temporal evolution of the lattice parameters and of the total film thickness together with the evolution of the RH are presented in Figs. 2 and 3, respectively. It can be seen in these figures that the response of the film to any change in RH is extremely fast. It actually occurs over a characteristic time of one second. This is well evidenced on the kinks observed in the RH curve related to our imperfect way of tuning of the RH. The same kinks are seen both on the lattice parameters and on the total film thickness. In particular, it is the interferometry measurements made over less than 1 s that fully support this statement. Concerning the long-term evolution, similarly to what we found in our previous study [10] (carried out in other RH conditions), we observe that the b lattice
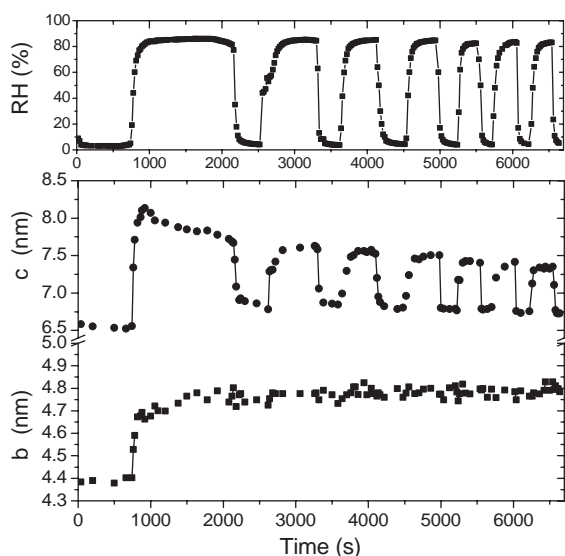
Fig. 2. Evolution of the RH and of the lattice parameters *b* and *c* as a function of time. The lattice parameters are described in the rectangular face centered unit cell.
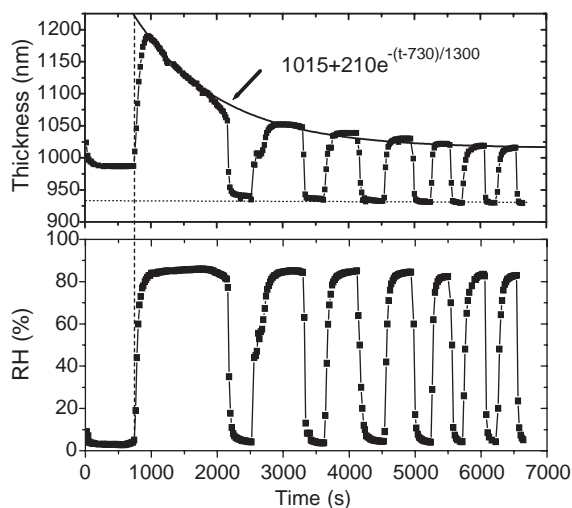

Fig. 3. Evolution of the total thickness of the film during the humidity cycles.

parameter does not behave the same way as the *c* lattice parameter. In particular, the first humidity cycle (up to 2000 s in Fig. 2) differs from subsequent cycles. During the first cycle *c* increases from 6.6 to 8 nm, whereas *b* increases from 4.3 to 4.8 nm. Since both lattice constants increase by

about the same 15% proportion there is no overall change in the shape of the unit cell. Along *b*, the 0.5 nm increase almost corresponds to the thickness of the water layer surrounding the micelle. Indeed the diameter of water can be estimated to be 0.31 nm from the cube root of the volume of a bulk water molecule so that 0.5 nm corresponds to nearly two layers of water, one on each side of the micelle as shown in Fig. 4. By considering the 10 nm [2] increase in the area of the unit cell and a 9.6 Å^2 area per water molecule, 104 water molecules of water are needed to cover the two micelles per unit length of water. Thus, in the 2D hexagonal plane there are 57 water molecules covering each micelle per unit length of water. The fact that about one layer of water is found to cover a micelle can be considered as an evidence of the micellar hydration. We do not explain why the lattice does not swell more than that upon increasing the RH but only accepts a coverage of one monolayer of water.

After the second drying stage we again increased the RH to ~85%. The *c* lattice parameter was found to rise again from 6.6 to 7.5 nm. After the first cycle, the system does not recover its full expansion along *z* direction because of the reduced flexibility of the silica network. By cycling over longer periods of time, *c* increases less and less as the silica network further condenses. During these cycles we also measured the total thickness of the film by optical interferometry. As shown in Fig. 3 one can see that the total thickness of the film
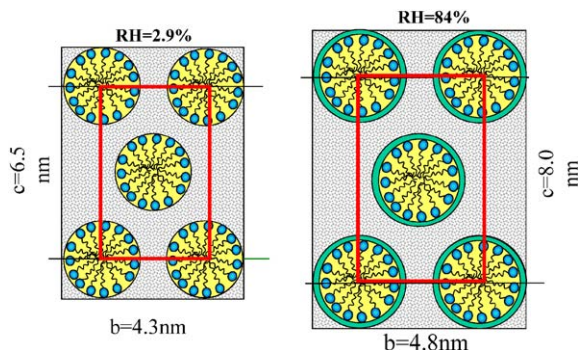

Fig. 4. Description of the 2D hexagonal lattice in the rectangular face centred unit cell before (left) and after (right) hydration of the micelles during the first RH cycle.

mimics the evolution of the c lattice parameter over a large period of time. This unambiguously proves that the entire film swells and contracts simultaneously. In addition, the evolution of the film thickness at high RH can be fitted with an exponential decay having a characteristic time of 1300 s. This shows that the evolution of the silica matrix responds over at least this period of time. Due to the exponential decay, we can see in Fig. 3 that the film is not yet fully stabilized after more than 2 h. As already pointed out by Grosso et al., these hybrid materials remain flexible for a certain amount of time corresponding to the modulable steady state (MSS) [11]. Actually this state can be decomposed in a fully flexible state (FFS) followed by an in-plane frozen state (IPFS) [10]. In this study of the long time response of these films, we have found that the IPFS extends for more than several hours. In this state, the film shrinks along the direction perpendicular to the film as a result of the silica condensation. The present study allows estimating that the time necessary to fully condense the silica in the IPFS is about 2 h.

4. Conclusion

GISAXS experiments were exploited to follow the evolution of the lattice constant with respect to RH. During the RH cycles, we have found that the lattice constant of the 2D hex phase mimics the evolution of the total film thickness measured by optical interferometry. During the first increase of RH, we found that the micelles get hydrated with one layer of water molecules for each micelle. In the following stage, this behavior is impeded by both the progressive condensation of the silica network and by the pinning effect. The long-term behavior of the silica condensation is experimentally described by following the evolution of the total thickness of the film versus time while cycling the RH.

Acknowledgements

References

[1] For a recent review see J.Y. Ying, C.P. Mehnert, M.S. Wong, Angew. Chem. (Int. Ed.) 38 (1999) 56.

[2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.

[3] J.S. Beck, J.C. Vartuli, M.E. Roth, W.J. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[4] Y. Lu, R. Cangull, C.A. Drewlen, M.T. Anderson, C.J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, Huang, J.I. Zing, Nature 389 (1997) 364.

[5] R. Ranganathan, M. Peric, R. Medina, U. Garcia, B.L. Bales, Langmuir 17 (2001) 6765.

[6] A. Gibaud, D. Doshi, B. Ocko, V. Goletto, C.J. Brinker, in: Park, et al. (Eds.), Studies in Surface Science and Catalysis, vol. 146, Elsevier, Amsterdam, 2003, pp. 351–354.

[7] D.A. Doshi, A. Gibaud, V. Goletto, M. Lu, H. Gerung, B. Ocko, S. Hang, C.J. Brinker, J. Am. Chem. Soc. 125 (2003) 11646.

[8] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.

[9] M. Klotz, P.A. Albouy, A. Ayral, C. Ménager, D. Grosso, A. Van der Lee, V. Cabuil, F. Babonneau, C. Guizard, Chem. Mater. 12 (2000) 1721.

[10] A. Gibaud, S. Dourdain, O. Gang, B. Ocko, PRB 70 (2004) 161403 (R).

[11] D. Grosso, A.R. Balkenende, P.A. Albouy, A. Ayral, H. Amenitsch, F. Babonneau, Chem. Mater. 13 (2001) 1848; Grosso, et al., Chem. Mater. 14 (2002) 931.